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Catalytic chemodivergent annulations between α-diketones and alkynyl α-diketones

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Four types of unprecedented and chemodivergent reactions between α-diketones and alkynyl α-diketones have been achieved under the catalysis of phosphine and Brønsted base, respectively, leading to the rapid construction of four different classes of biologically important but synthetically challenging molecular scaffolds including 2-hydroxyfuran-3(2H)-ones, 4-hydroxy-2-oxabicyclo[2.2.1]heptan-3-ones, 1,3-diaryl cyclobutanes, and 4-(furan-2(3H)-ylidene)cyclopent-2-enones. The formation of the products includes two novel rearrangement processes, and further transformations on the products can be easily achieved to deliver value-added substances such as highly functionalized cyclopentanes. Moreover, the 2-hydroxyfuran-3(2H)-one products display promising photophysical properties such as green luminescence under UV light and aggregation-induced emission effect, showing the practical application value of this work. The great potential of α-diketones in both synthetic chemistry and material science has been unambiguously demonstrated.

chemodivergent reaction, cascade annulation, phosphine catalysis, rearrangement reaction, fluorescent material

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1 Introduction

Reactions occurring *via* unprecedented mechanisms that can facilitate the rapid construction of biologically important scaffolds are highly valuable since they lead to revolutionary techniques through significantly shortening synthetic steps, reducing production cost, and enhancing the efficiency of the whole process. On the other side, using the same set of starting chemicals to undergo chemodivergent transformations and furnish thoroughly different molecular skeletons through only slightly changing the reaction conditions is also a highly desired research topic, especially when the products are all valuable substances but not easily accessible *via* known approaches [1]. In this context, rearrangement reactions serve as a nice choice to achieve the above purpose owing to the ability of unconventional bond cleavage and formation [2]. However, in most cases, a reaction can only proceed *via* one type of mechanism and tuning the reaction to happen *via* distinct processes and afford valuable molecules is absolutely very challenging, especially when two types of

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rearrangement mechanisms are involved.

For instance, 2-hydroxyfuran-3(2H)-ones (HFO), 4-hydroxy-2-oxabicyclo[2.2.1]heptan-3-ones (HBHO), and 1,3-diaryl cyclobutanes (DCB) are three types of thoroughly different skeletons that widely exist in natural products such as (*E*)-siphonarienfuranone [3a], scopranone A/B [3b], linfuranone A/B/C [3c], AS-183 [3d], JBIR-108 [3e], illisimonin A [3f]], norcrassin A [3g], preuisolactone [3h], langduin D [3j]], fischeriana A [3j], piperarborenine D [3k], anthocertotonic acid [3l], katsumadain C [3m], and they have shown a large variety of promising bioactivities such as anti-Alzheimer's disease activities, antibacterial activity against micrococcus luteus, growth-inhibitory effects effects against human hepatic liver carcinoma cells, *in vitro* cytotoxicity against P-388, HT-29, and A549 cancer cell lines, neuroprotective effects against oxygen-glucose deprivation-induced cell injury in SHSY5Y cells, *etc*. (Figure 1(a–c)) [3]. Additionally, 4-(furan-2(3H)-ylidene)cyclopent-2-enone (FCE) core structure exists in Maillard type chromophores and has been found to show antiproliferative property (Figure 1(d)) [3n].

However, the synthesis of these frameworks is not easy. For the HFO type molecules, the widely used strategy is the oxidation of 1,2,4-triol precursors to the corresponding triketones, and the simultaneous annulations afford HFO compounds (Scheme 1(a)) [3b,3e,4a]. This protocol employs multiple steps for the synthesis of 1,2,4-triols, which often results in low yields. For the HBHO skeletons, no concise approach has been developed. Danishefsky and co-workers [4b] reported a ten-step synthesis of the HBHO framework towards terreulactone A using an intramolecular bromolactonization as the key step (Scheme 1(b)). Recently, Rychnovsky and Burns [4c] completed the total synthesis of illisimonin A in 14 steps, and the last step was the final HBHO skeleton formation, which used a novel C–H bond activation method (Scheme 1(c)). For the DCB skeletons, the widely used strategy is photo-catalyzed [2+2] annulation, but in most cases, *trans*-1,3-diaryl or *cis*-1,2-diaryl cyclobutanes are formed, leaving *cis*-1,3-diaryl ones less available (Scheme 1(d)) [5]. To solve this trouble, an elegant stereocontrollable synthesis of both *trans*- and *cis*-DCBs has been developed by Baran and co-workers [6] using C–H bond activation (Scheme 1(e)).

We have been interested in α-diketone chemistry, with the aim of systematically investigating and disclosing the unique features related to α-diketone compounds, which are thoroughly distinct from the known reaction modes using common ketones and unsaturated ketones [7]. Here we illustrate four types of unprecedented annulations between α-diketones and alkynyl α-diketones catalyzed by phosphine and Brønsted base, respectively, and the reactions afford synthetically challenging but valuable HFO, HBHO, DCB, and FCE skeletons all in one-step fashions. A series of functional group transformations are achieved in the processes and two types of novel rearrangement mechanisms are involved.

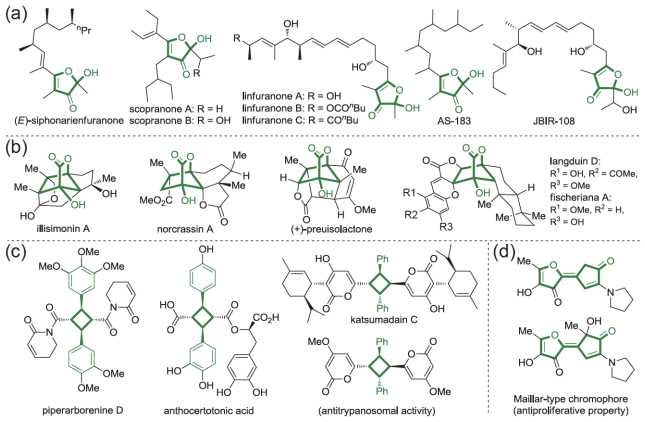
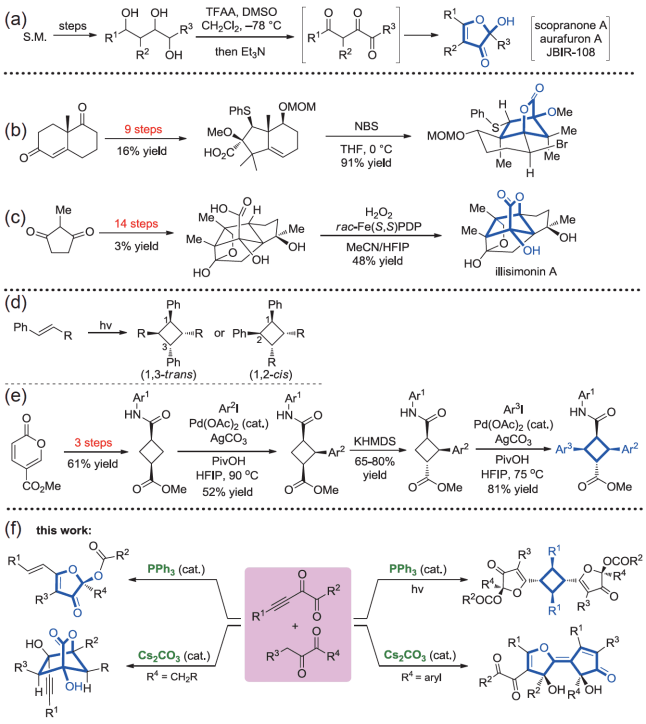


Figure 1 Bioactive natural products containing HFO (a), HBHO (b), DCB (c), and FCE (d) skeletons (color online).



Scheme 1 Synthetic methods towards HFO, HBHO, and DCB skeletons. (a) Known method for the synthesis of HFO. (b) Danishefsky's method for the synthesis of HBHO. (c) Rychnovsky and Burns' method for the synthesis of HBHO. (d) [2+2] annulation of styrene. (e) Baran's method for the synthesis of cis-1,3-diaryl cyclobutane. (f) This work (color online).

2 Experimental

2.1 General procedure for the synthesis of HFO skeletons

Substrate **1** (0.2 mmol), **2** (0.24 mmol), and PPh_3 (0.04 mmol) were added to MeOH (1 mL) at room tem-

perature under argon atmosphere. The reaction system was kept in dark place and stirred at room temperature for 5 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, *v*:*v* = 30:1) to give the product **3**.

2.2 General procedure for the synthesis of HBHO skeletons

Substrate **1** (0.4 mmol), **2** (0.48 mmol), and PPh_3 (0.08 mmol) were added to MeOH (1 mL) at room temperature under argon atmosphere. The reaction system was stirred at room temperature for 5 h. Then toluene (1 mL) was added to the reaction system and the reaction mixture was stirred for 48 h under the light. The light source used in this procedure is a standard 36 W floodlight. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, *v*:*v* = 5:1) to give the product **4**.

2.3 General procedure for the synthesis of DCB skeletons

Substrate **1** (0.2 mmol), **2** (0.24 mmol), and Cs_2CO_3 (0.04 mmol) were added to toluene (1 mL) at room temperature under argon atmosphere. The reaction system was stirred at room temperature for 5 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, *v*:*v* = 10:1) to give the product **5**.

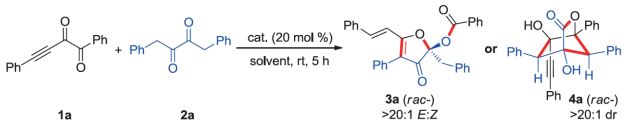
2.4 General procedure for the synthesis of FCE skeletons

Substrate **1** (0.8 mmol), **2** (0.2 mmol), and Cs_2CO_3 (0.04 mmol) were added to toluene (1 mL) at 45 °C under argon atmosphere. The reaction system was stirred for 7 h. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, *v*:*v* = 5:1) to give the product **6**.

3 Results and discussion

As shown in Table 1, we initially tested the reactions of easily available **1a** and **2a** using PPh_3 as the catalyst. To our delight, the reaction in toluene afforded 2-hydroxyfuran-3(2H)-one **3a** in 63% yield (Table 1, entry 1), and the product is formed through a formal CO−CO bond cleavage within **1a** and a O−COPh bond formation in the product. Moreover, the triple bond in **1a** has been converted to a double bond with only *E*-isomer detected. Phosphine organocatalysis has proved a powerful synthetic tool in achieving unconventional transformations *via* various annulation reactions [8], and the activation of alkynyl carbonyls *via* phosphine catalysis has also been well studied [9]. But to the best of our knowledge, such a conversion leading to 2-hydroxyfuran-3(2H)-one product has been not achieved. Considering that **3a** represents a highly valuable frame structure in bioactive substances, we continued to optimize the yield through screening solvents. A higher yield of 81% was obtained when CH_2Cl_2 was used (Table 1, entry 2), but lower yields were observed when CH_3CN, tetrahydrofuran (THF), and 1,4-dioxane were tested (Table 1, entries 3−5). We were glad to find that the protic solvent of MeOH can produce **3a** in quantitative yield (Table 1, entry 6). To our pleasure, a thoroughly different product of **4a** was identified when we surveyed Brønsted base catalyst such as K_2CO_3, and the reaction generated 4-hydroxy-2-oxabicyclo[2.2.1]heptan-3-one **4a** as the only product (Table 1, entry 7). Again the mechanism of the formation of **4a** seems very interesting, and one of the two benzyl groups in **2a** undergoes cleavage, followed by a two-fold attack of the carbonyl groups together with an ester group formation. As has been shown in Scheme 2(c), currently there is no simple way to construct HBHO

Table 1 Condition optimization for divergent formation of **3a** and **4a**[a] (color online)



entry	cat. (mol %)	solvent	yields (%)	
			3a	**4a**
1	PPh_3 (20)	toluene	63	–
2	PPh_3 (20)	CH_2Cl_2	81	–
3	PPh_3 (20)	CH_3CN	61	–
4	PPh_3 (20)	THF	34	–
5	PPh_3 (20)	1,4-dioxane	17	–
6	PPh_3 (20)	MeOH	99	–
7	K_2CO_3 (20)	toluene	–	37
8	KOH (20)	toluene	–	29
9	K_3PO_4 (20)	toluene	–	45
10	Cs_2CO_3 (20)	toluene	–	74
11	Cs_2CO_3 (20)	CH_2Cl_2	–	38
12	Cs_2CO_3 (20)	CH_3CN	–	56
13	Cs_2CO_3 (20)	THF	–	65
14	Cs_2CO_3 (20)	MeOH	–	45
15	Et_3N (20)	toluene	–	trace
16	DBU (20)	toluene	–	trace

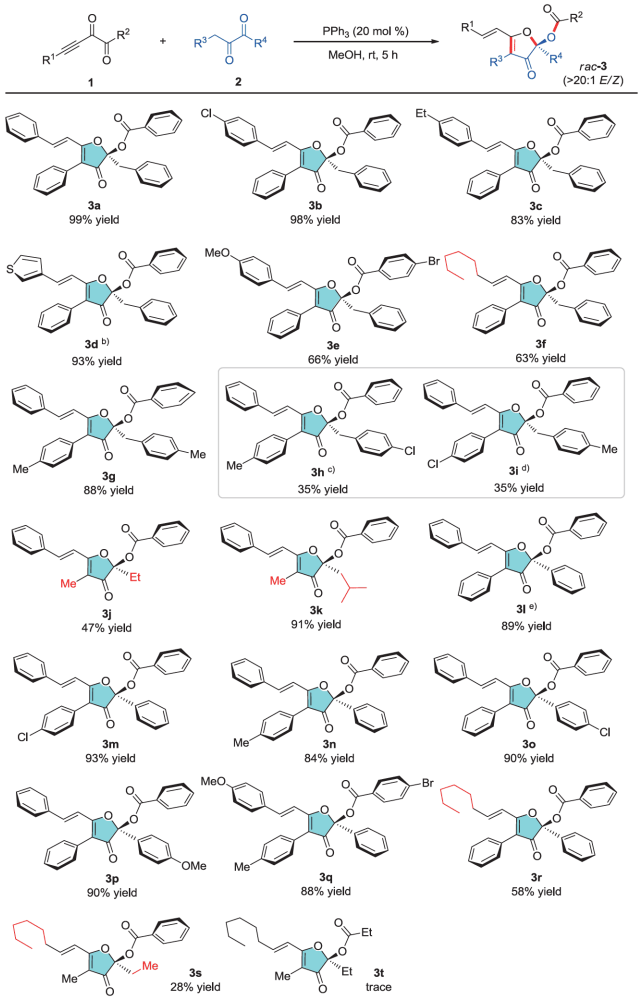
a) Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), cat. (20 mol%), solvent (1 mL), rt, 5 h, under argon atmosphere. The diastereomeric ratio was determined *via* ^{1}H NMR analysis of the reaction mixtures. All yields were isolated yields based on **1a**.

skeleton efficiently. Therefore, this reaction provides an excellent solution to the issue. Other bases of KOH and K_3PO_4 could also produce **4a**, but in low yields (Table 1, entries 8 and 9). However, Cs_2CO_3 is proved suitable for the reaction, affording **4a** in 74% yield (Table 1, entry 10). Using Cs_2CO_3 as the base, we screened some other solvents such as CH_2Cl_2, CH_3CN, THF, and MeOH, and in all cases, **4a** was obtained, albeit in lower yields (Table 1, entries 11−14). Organic bases such as Et_3N and DBU were also tested but gave only a trace amount of the product (Table 1, entries 15 and 16).

Having identified the optimal conditions for the divergent formation of **3a** and **4a**, we commenced to study the generality and limitations of the protocol, with the formation of HFO **3** investigated first. Using **2a** as one of the reactants, we surveyed a range of alkynyl diketones with different aromatic substituents and found that the reaction tolerated phenyl rings with both electron-withdrawing and electron-donating groups (Table 2, **3b** and **3c**), and heterocyclic thienyl substituent showed little effect on the results (Table 2, **3d**). The simultaneous change of the two substituents of the alkynyl diketone substrate was also proved feasible, affording **3e** in 66% yield (Table 2, **3e**). To our pleasure, an aliphatic group was also compatible with the reaction conditions, leading to **3f** in 63% yield (Table 2, **3f**). Subsequently, we studied the scope of diketones **2** in the reaction, and symmetrical 4-MeC_6H_4 substituted diketone worked well to give **3g** in high yield (Table 2, **3g**). However, the unsymmetrical diketone bearing 4-MeC_6H_4/4-ClC_6H_4 groups (**2c**) did not show good regioselectivity, and the corresponding products **3h** and **3i** were gotten in equal yields (Table 2, **3h** and **3i**). The NMR analysis shows that both α-positions of **2c** are acidic enough to form the corresponding enols, and are not apparently affected by the existence of Cl and Me groups in the phenyl rings. Moreover, diketones with only alkyl groups were found suitable for the reaction, resulting in the formation of **3j** and **3k** in reasonable yields (Table 2, **3j** and **3k**). Noteworthy is that excellent regioselectivity was observed in the formation of **3k**. Then we were glad to see that diketones with phenyl/benzyl type substituents reacted well with aromatic alkynyl diketones, affording **3l**−**3q** all in high to excellent yields (Table 2, **3l**−**3q**). **3r** and **3s** with one or three aliphatic substituents could also be formed, albeit in 58% and 28% yields, respectively (Table 2, **3r** and **3s**). Noteworthy is that in most cases, product **3** was obtained with >20:1 *E*/*Z* ratio. The attempts to get **3t** with four aliphatic groups failed despite the full consumption of the starting materials, which is probably owing to the instability of the product (Table 2, **3t**).

To our delight, the HFO compounds with the exocyclic double bonds were found to undergo [2+2] annulations under photo-irradiation to afford *cis*-1,3-diary cyclobutane (DCB) compounds bearing two heterocyclic furanone rings. Ana-

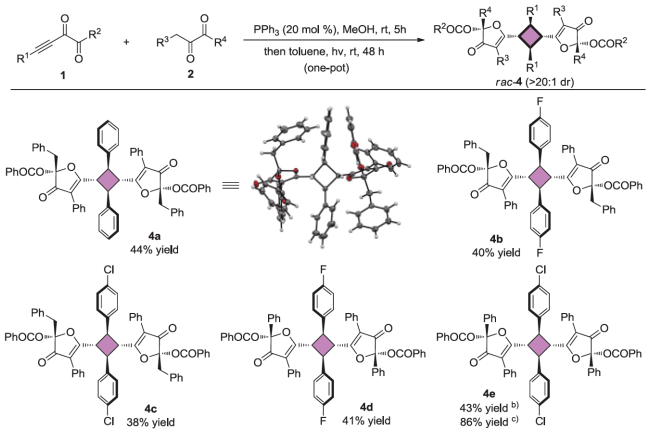
Table 2 Scope of HFO formation [a] (color online)



a) Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), PPh_3 (20 mol%), MeOH (1 mL), rt, 5 h, under argon atmosphere. All yields were isolated yields based on **1**. b) *E*/*Z* = 10:1. c) *E*/*Z* = 18:1. d) *E*/*Z* = 19:1. e) *E*/*Z* = 14:1.

logous compounds have shown promising bioactivities [3m], which inspired us to further study the possibility of getting DCB products in a one-pot fashion. A rough screening showed that the reaction of **1a** and **2a** under PPh_3 catalysis first in dark for 5 h then under the irradiation of a 36 W floodlight for 48 h furnished **4a** in 44% yield with >20:1 dr (Table 3, **4a**). The structure of **4a** was confirmed unambiguously *via* single-crystal X-ray analysis. Then we tested the generality of affording such 1,3-diaryl cyclobutanes and found that products with fluoro- and chloro-phenyl groups could all be obtained with excellent diastereoselectivities in moderate yields (Table 3, **4b**–**4e**). Noteworthy is that the 1,3-diaryls and the 2,4-difuranones are all in *cis*-configuration, which has been less achieved in known reports [5]. The moderate yields were due to the relatively low reaction rate. As shown in product **4e**, 29% yield of the monomer **3b** was also isolated together with the formation of **4e**, and the yield could be increased to 86% when the reac-

Table 3 Scope of DCB formation [a] (color online)



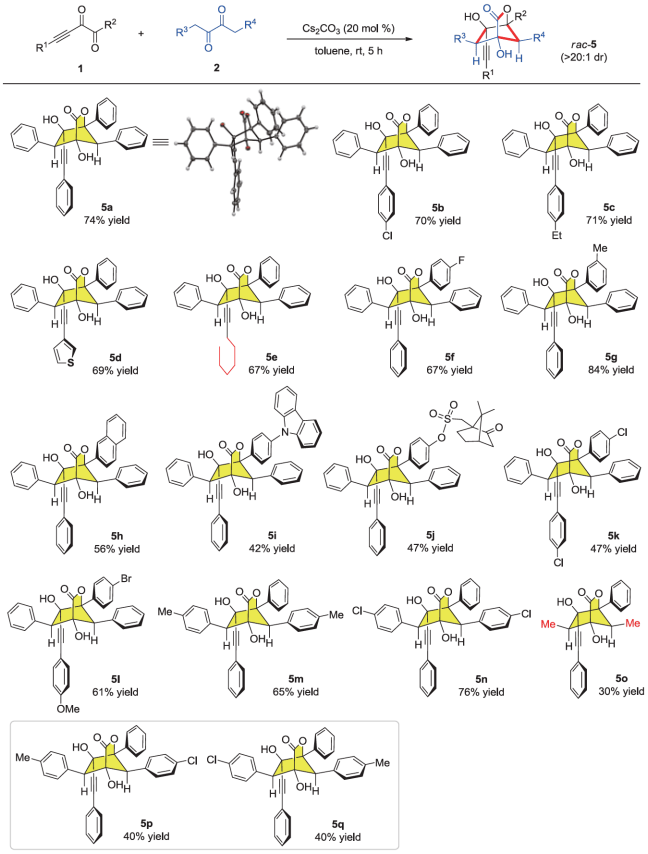
a) Reaction conditions: **1** (0.4 mmol), **2** (0.48 mmol), PPh_3 (20 mol%), MeOH (1 mL), 5 h, then toluene (1 mL), 36 W floodlight irradiation, rt, 48 h, under argon atmosphere. The diastereomeric ratios were determined *via* ^{1}H NMR analysis of the reaction mixtures. All yields were isolated yields based on **1**. b) *E*-**3b** and *Z*-**3b** were isolated in 29% yield with the ratio of 3:1. c) The reaction was run for 4 days.

tion was run for 4 days. Moreover, both *E*- and *Z*-isomers of **3b** were observed with the ratio of 3:1, indicating the presence of a fast *E*- to *Z*-isomerization and the *Z*-isomer might be the real dimerization-active substrate.

Then we focused on the catalytic formation of HBHO skeleton, which also widely exists in bioactive molecules [3e–3j], but no one-step construction of HBHO skeletons has been revealed to date. First, we tested a series of alkynyl diketones with different R^1 groups, and found that 4-ClC_6H_4, 4-EtC_6H_4, thienyl, and aliphatic ^{n}C$_6$H$_{13}$ groups were all tolerated under the optimal conditions, delivering the corresponding bicyclic products in 67%–71% yields (Table 4, **5b**–**5e**). Then we observed that the variation of the R^2 was also possible, and phenyl rings bearing different substituents (4-F and 3-Me) and naphthyl group all showed little effect on the results (Table 4, **5f**–**5h**). Furthermore, the introduction of a carbazole group and a camphorsulfonyl group into the phenyl ring could also produce the products, albeit in lower yields (Table 4, **5i** and **5j**). The simultaneous change of both R^1 and R^2 groups was proved possible, allowing access to **5k** and **5l** in moderate yields (Table 4, **5k** and **5l**). Moreover, diketones **2** with both electron-rich and electron-poor aromatic rings underwent smooth rearrangement-annulations to produce **5m** and **5n** in moderate to good yields (Table 4, **5m** and **5n**), and diketones without aromatic substituents such as hexane-3,4-dione were also suitable reactant to generate the corresponding lactone **5o**, albeit in low yield (Table 4, **5o**). An unsymmetrical nucleophilic diketone was also tested, but showed poor regioselectivity, giving both **5p** and **5q** in a 1:1 ratio (Table 4, **5p** and **5q**).

Under the catalysis of Cs_2CO_3, when the R^4 unit in substrate **2** is a phenyl group, the bridged lactone cannot be formed. Instead, a three-component reaction happens to deliver **6a** as the major product (Table 5, **6a**). The molecular complexity is constructed by two equivalents of **1a** and one equivalent of **2a**. The reaction tolerated aromatic R^4 groups bearing different substituents such as 4-Cl and 4-Me groups, releasing **6b** and **6c** in 33% and 40% yields, respectively (Table 5, **6b** and **6c**). Furthermore, alkynyl diketones with 3-F-C_6H_4 substituent at the R^1 unit also underwent the annulation to produce **6d** (Table 5, **6d**). The relatively low yields were owing to the partial decomposition of **2** under the reaction conditions. However, 4-Cl–C_6H_4 group at the alkynyl moiety showed better results for the yield, generating **6e** and **6f** in 66% and 78% yields, respectively (Table 5, **6e** and **6f**). The structure of **6f** was identified *via* single-crystal X-ray structure analysis.

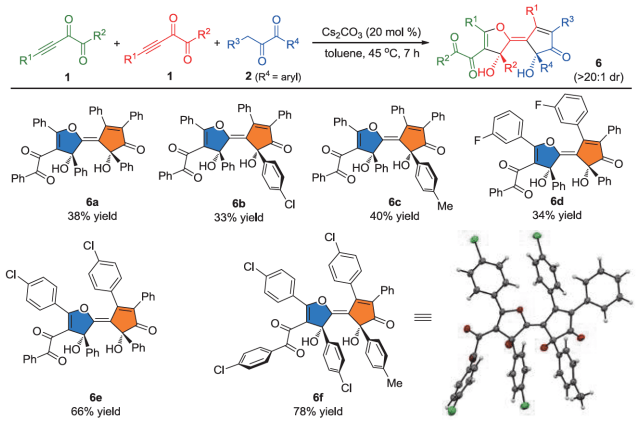
Table 4 Scope of HBHO formation [a] (color online)



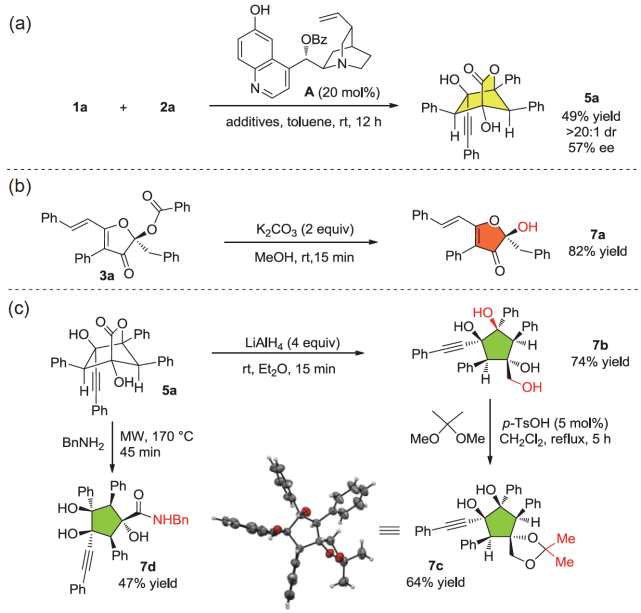
a) Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), Cs_2CO_3 (20 mol %), toluene (1 mL), rt, 5 h, under argon atmosphere. The diastereomeric ratios were determined *via* ^{1}H NMR analysis of the reaction mixtures. All yields were isolated yields based on **1**.

Preliminary studies on the asymmetric synthesis of **5a** have been conducted using chiral amines (see the Supporting Information online for more details), and promising results were obtained using catalyst **A**, which led to **5a** in 49% yield with >20:1 dr and 57% ee (Scheme 2(a)). A series of further transformations on the products can also be easily achieved. For instance, the hydrolysis of **3a** under basic conditions afforded **7a** in 82% yield (Scheme 2(b)). The $LiAlH_4$ re-

Table 5 Scope of FCE formation [a] (color online)



a) Reaction conditions: **1** (0.8 mmol), **2** (0.2 mmol), Cs_2CO_3 (20 mol%), toluene (1 mL), 45 °C, 7 h, under argon atmosphere. The diastereomeric ratios were determined *via* ^{1}H NMR analysis of the reaction mixtures. All yields were isolated yields based on **2**.



Scheme 2 Asymmetric formation of **5a** and synthetic applications of the products. (a) Asymmetric synthesis of **5a**. (b) Hydrolysis of **3a**. (c) Further transformations on **5a** (color online).

duction of **5a** furnished highly functionalized cyclopentane **7b** in 74% yield, and further selective protection of the diol unit provided **7c**, which was confirmed *via* single-crystal X-ray structure analysis; moreover, the reaction of **5a** with $BnNH_2$ led to amide **7d** (Scheme 2(c)). Cyclopentanes have served as useful building blocks in organic synthesis and are ubiquitous in bioactive substances [10]. Therefore, these reactions provide a useful method for the rapid construction of highly functionalized cyclopentane analogues.

Organic fluorescent materials have attracted intense research focus because of their wide applications in organic light-emitting diodes (OLEDs), fluorescent sensors, semiconductor lasers, *etc*. [11]. However, many organic materials exist aggregation-caused quenching (ACQ) problem, which has greatly restricted the corresponding practical applications because fluorescent materials are usually used in the aggregated or solid state [12]. The discovery of materials with aggregation-induced emission (AIE) properties perfectly solves the problem and has found wide uses in many fields such as biosensors, DNA visualizers, optical waveguides, liquid crystals [13]. In this context, the exploitation of new types of organic solid luminophores with AIE properties has been one of the core missions in the field. We are delighted to find that many of the 2-hydroxyfuranone products **3** such as **3p**, **3d**, **3a**, **3l**, **3n**, and **3g** show bright green fluorescence under UV light (Figure 2(a)), clearly showing the real application potential of this work. Furthermore, an obvious AIE effect was also observed. For instance, when water was added into the CH_3CN solution of **3f**, **3p**, and **3g**, the strongest fluorescent emission was detected at 70%, 90%, and 90% of the water concentration, respectively (Figure 2(b)). We also tested the absorption spectra (Figure 2(c)) and emission spectra (Figure 2(d)) of the above selected emissive molecules. The UV-vis absorption peak of solid molecules **3** ranged from 378 to 426 nm, and the fluorescence emission ranged from 524 to 545 nm correspondingly. To the best of our knowledge, such a vinyl hydroxyl furanone molecular skeleton has been not disclosed to show promising photophysical properties, and this work represents the first example.

The postulated mechanisms forming **3a**, **4a**, **5a**, and **6a** are demonstrated in Scheme 3. As has been shown in Scheme 3 (a), the nucleophilic addition of PPh_3 to **1a** leads to allenolate intermediate **I-1**, which has a resonance structure of **I-2**. The

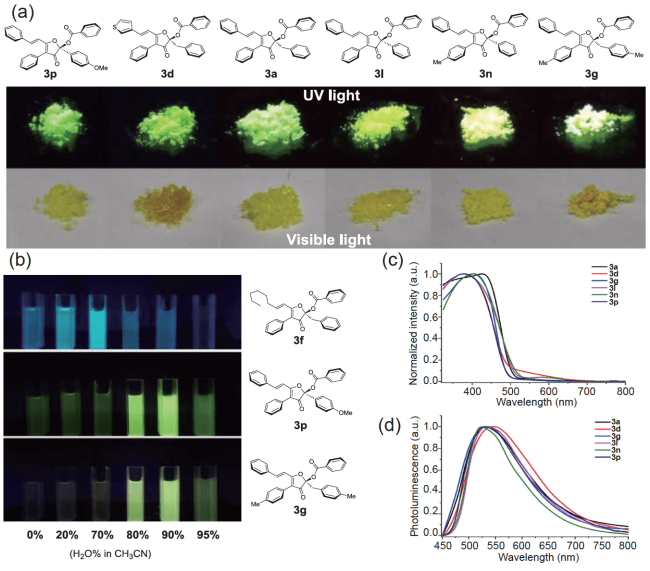
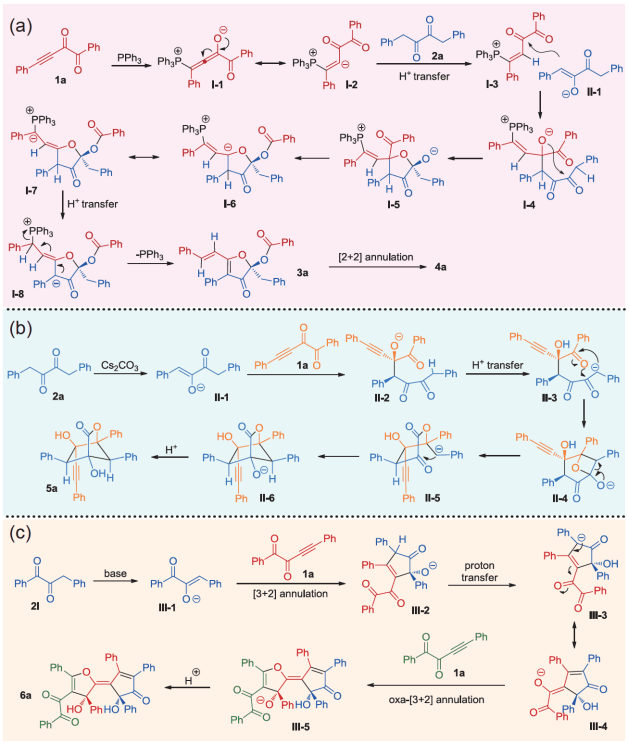


Figure 2 (a) Selected illuminant compounds under visible light and ultraviolet irradiation at 365 nm. (b) The AIE effect of selected **3**. (c) The UV-Vis absorption spectra of selected **3** as amorphous powders (T = 298 K). (d) The emission spectra of selected **3** as amorphous powders (T = 298 K, excited at the respective λ_{max} 440 nm) (color online).



Scheme 3 Postulated mechanism leading to **3a** and **4a** (a), **5a** (b) and **6a** (c). (color online).

proton transfer from **2a** to the allenolate affords **I-3** and **II-1**, and an aldol reaction happens to give **I-4**, which is followed by an intramolecular oxygen anion attack of the diketone moiety to release **I-5**. An acyl transfer happens to produce **I-6**, which has a resonance structure of **I-7**. The second proton transfer occurs to generate enolate **I-8**, and after the release of PPh_3, **3a** is formed. Under irradiation conditions, an intermolecular [2+2] annulation can happen, allowing access to cyclobutane **4a**.

In sharp contrast, the reaction of alkynyl diketone **1a** and diketone **2a** under the catalysis of Cs_2CO_3 undergoes a thoroughly different mechanism (Scheme 3(b)). Enolate **II-1** attacked the internal ketone moiety of **1a** to furnish **II-2**, which was followed by a proton transfer to yield a new enolate **II-3**. An intramolecular formal [2+2] annulation liberates **II-4**, which is very unstable and prefers to undergo a C–C bond cleavage to provide α-ketoester **II-5**. Then after an intramolecular ring-closure and proton transfer, the final bridged lactone **5a** is formed.

For comparison, when **2l** is used as the nucleophile, because the second enolate such as **II-3** cannot be formed, the reaction undergoes another mechanism. A formal [3+2] annulation happens between **III-1** and **1a** to produce **III-2**, and after proton transfer, enolate **III-3** forms, which has a resonance structure of **III-4**. Then an oxa-[3+2] annulation occurs between **III-4** and the second molecule of **1a** to afford bicycle intermediate **III-5**, and after proton transfer, **6a** is obtained.

4 Conclusions

In summary, we have systematically studied the reactions between α-diketones and alkynyl α-diketones under the catalysis of phosphine and Brønsted base, respectively. Four different types of unprecedented annulations have been disclosed, and a series of biologically important but synthetically challenging molecular scaffolds, such as 2-hydroxyfuran-3(2H)-ones, 4-hydroxy-2-oxabicyclo[2.2.1]heptan-3-ones, 1,3-diaryl cyclobutanes, and 4-(furan-2(3H)-ylidene)cyclopent-2-enone were easily obtained in a one-step fashion. Such chemodivergent transformations affording four useful molecular scaffolds have been scarcely reported. Furthermore, two different rearrangement mechanisms, regio- and stereoselective *cis*-1,3-diaryl cyclobutane formation, and further transformations affording highly functionalized cyclopentanes were also highlighted in this work. Moreover, the 2-hydroxyfuran-3(2H)-one products display promising photophysical properties such as green luminescence under UV light, and aggregation-induced emission effect, showing the practical application value of this work. The unique chemistry associated with α-diketones has been clearly demonstrated, indicating the great potential of this field in both synthetic chemistry and material science. More systematic investigations on α-diketone chemistry are ongoing in our group and will be reported in due course.

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Conflict of interest The authors declare no conflict of interest.

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